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Application of Box Behnken design to Optimize the Reaction Conditions on the Synthesis of Multiwalled Carbon Nanotubes

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Abstract

This paper describes the use of Box Behnken design approach to plan the experiments for turning the yield of Multiwalled Carbon nanotubes (MWCNTs) synthesis by spray pyrolysis method using Citrus limonum oil as carbon precursor and Fe/Co supported on silica as catalyst. Reaction temperature, composition of catalyst and feed rate of precursor were the chosen parameters to optimize the process. A total of 17 runs were required to achieve the optimum conditions. Characterization of as grown CNTs were done by scanning electron microscopy, Transmission electron microscopy and Raman Spectroscopy. This work resulted in identifying the optimized set of turning parameters for spray pyrolysis to achieve high yield of CNTs.

Keywords: *Box-Behnken design, Carbon nanotube, Spray pyrolysis.*

1. INTRODUCTION

Carbon nanotubes are members of the fullerene structural family that was discovered by Iijima in 1991(Iijima, 1991). These incredible structures have enthralling mechanic, electronic and magnetic properties (Langer *et al.* 1996; Yu *et al.* 2000; Dressel Haus *et al.* 2001). These peculiar properties makes the material potentially applied in solar cells, nanoelectronic devices, field emitters, gas storage, biosensors and as catalyst supports (Suzuki *et al.* 2003; Brattas *et al.* 2008; Yoon *et al.* 2005; Dillon *et al.* 1997; Oh *et al.* 2009 ; Pan *et al.* 2006). There are several methods for synthesis of CNTs, most widely used among them are Arc discharge, Laser ablation, Chemical vapour deposition and spray pyrolysis method (Song *et al.* 2007, Guo *et al.* 1995; Suriani *et al.* 2009; Ghosh *et al.* 2007; Kalaiselvan *et al.* 2014). Spray pyrolysis is similar to CVD and the only difference it is a single step process, whereas in CVD it is two step processes (Kalaiselvan *et al.* 2013; 2016). Catalysts such as Fe, Co or Ni catalysts were widely used for the synthesis of singlewalled and multiwalled CNTs (Kalaiselvan *et al.* 2016). Synergetic effect of the metals involved in the catalyst found to enhance the catalyst activity (Ghosh *et al.* 2008). Li *et al.* have studied the effect of temperature on growth and structure of carbon nanotubes (Li *et al.* 2002). Natural hydrocarbons have been utilized as carbon precursor for the synthesis of CNTs such as camphor, turpentine oil, pine oil, *Cymbopogen flexuous* oil and *Helianthus annuus* oil (Afre *et al.* 2006; Kumar *et al.* 2007; Karthikeyan *et al.* 2010; Mageswari *et al.* 2014; Angulakshmi *et al.* 2013). These natural precursors are very cheap, renewable and ample of its availability. Recently, process optimization with the aid of design of experiments is rapidly gaining popularity in various field related to nanotechnology. Nourbakhsh studied the effect of process parameters on the diameter of carbon nanotubes utilizing RSM (Nourbakhsh *et al.* 2007). Statistical design of experiment is the science of statistically analyzing the largest possible amount of information with the smallest number of experiments (Goh *et al.* 2001). Liu etal., optimized the reaction conditions for the synthesis of single-walled carbon nanotubes using reponse surface methodology (Liu *et al.* 2012). Box-Behnken designs were introduced in order to reduce the sample size as the number of parameters grows. Box-Behnken is based on a spherical, revolving design. It has been applied for the

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optimization of several chemical and physical processes, and the number of experiments is decided accordingly. In this study, the experiments were planned and conducted according to a Box-Behnken type response surface design. Box-Behnken experimental design is applied to investigate and optimize the reaction conditions, which affect the yield and morphology of CNTs.

2. EXPERIMENTAL METHODS

2.1 Preparation of mixture of catalysts

The preparation of Fe/ Co supported on silica was conducted using wet impregnation method. Fe/Co catalyst supported on silica (SiO_2) particles (Fe: Co: SiO_2 =1:0.4:4) were prepared as follows. Metal salts (Merck) i.e. Fe $(NO_3)_3$. $6H_2O$ and $Co(NO_3)_2.6H_2O$ were dissolved in methanol and mixed thoroughly with methanol suspension of silica (Merck). The solvent was then evaporated and the resultant cake heated to 90-100° C for 3 hours, removed from the furnace and ground in an agate mortar. The fine powders were then calcined for 1 hour at 450° C and then re-ground before loading into the reactor.

2.2 Fabrication and purification of nanotubes

The synthesis of Multiwalled Carbon nanotubes (MWCNTs) was carried out using a spray pyrolysis method. The catalyst was placed on the quartz boat. The boat was placed in the heating furnace. In this experiment, the quartz tube was first flushed with nitrogen in order to remove air and create nitrogen atmosphere and then heated to a reaction temperature. The precursor solution of *Citrus limonum* oil was sprayed into the quartz tube using nitrogen as a carrier gas. The experiments were conducted by varying the process parameters with a reaction time of 45 minutes. After cooling down to room temperature in flowing nitrogen gas, carbon deposit was removed from the reactor and weighed. The yield of carbon deposit was calculated according to Willems *et al.* (2000) as, Carbon deposit % = 100 $(m_{Total} – m_{Cat})/m_{Cat}$, where m_{Cat} is the initial amount of catalyst and m_{Total} is the total mass of the sample after the reaction. The as-grown products were heated with 1N HCl at 60°C for 30 min. Finally the samples were washed with distilled water to remove the acid. The collected sample was dried at 120°C in air for 2 hours.

As grown carbon samples surface morphology was examined using scanning electron microscope and high–resolution transmission electron microscope. The crystalline structure of CNT samples was characterized by Raman Spectroscopy.

2.3 Experimental Design

Box-Behnken experimental design, is a three level design based on the combination of a factorial design. For this approach, Design-Expert Software version 8, Stat-Ease was used to design the experiment and randomize the runs. Box Behnken designs allow estimating coefficients in a second degree polynomial regression and modeling of a quadratic response surface. In the present investigation reaction temperature, composition of (Fe-Co) catalyst and feed rate of precursor was considered as input variables whereas, the percentage of yield was chosen as the response variable. Table 1 shows the highest and lowest levels of independent variables. The experimental design matrix by the Box-Behnken design for the *Citrus limonum* oil is tabulated in Table 2 and the corresponding experiments were performed.

Table 1. The Experimental Range and Levels of the Input Variables for *Citrus limonum* Oil

Input Variables	Level (-1)	Level (+1)
A:Reaction Temperature (°C)	550	750
B: Composition of Catalyst (g)	0.25	0.75
C: Feed rate of Precursor (mL)	10	30

Table 2. Box-Behnken Design Matrix and Corresponding Response for *Citrus limonum* Oil

	Factor 1	Factor 2	Factor 3	Response 1
Run	A: Reaction Temp (°C)	B: Catalyst Composition (g)	C: Feed rate of Precursor (mL)	Yield (%)
1	-1	0	-1	15
2	0	1	1	60
3	1	1	0	55
4	-1	0	1	35
5	0	0	0	78
6	0	1	-1	40
7	0	0	0	75
8	0	0	0	76
9	1	0	-1	42
10	0	0	0	72
11	0	0	0	71
12	-1	1	0	20
13	-1	-1	0	10
14	1	-1	0	50
15	0	-1	-1	37
16	0	-1	1	50
17	1	0	1	45

3. RESULTS & DISCUSSION

3.1 Box-Behnken Design and Data Analysis

Table 3: ANOVA for RSM parameters fitted to a polynomial equation for methyl ester of *Citrus limonum* oil

	Sum of Squares	df	Mean Square	F-Value	p-value Prob > F
Model	7195.064706	9	799.4516	24.6853	< 0.0001
A-Temperature	1568	1	1568	48.4164	0.0002
B-Catalyst composition	98	1	98	3.02602	0.1255
C-Feed rate of carbon precursor	392	1	392	12.1041	0.0103
AB	6.25	1	6.25	0.19298	0.6737
AC	72.25	1	72.25	2.23092	0.1789
BC	12.25	1	12.25	0.37825	0.5580
A^2	2973.602632	1	2973.603	91.8183	< 0.0001
B^2	834.1289474	1	834.1289	25.7560	0.0014
C^2	775.9184211	1	775.9184	23.9586	0.0018
Residual	226.7	7	32.38571		
Lack of Fit	193.5	3	64.5	7.77108	0.0382
Pure Error	33.2	4	8.3		
Cor Total	7421.764706	16			

Reaction temperature (°C), Composition of catalyst (g) and Feed rate of precursor (mL) were considered as independent process variables, and their individual and interactive effects on the yield percentage (as a response) of MWNTs were investigated using the Box-Behnken design approach. The quadratic equation for predicting the optimal point was achieved according to the Box-Behnken experimental design and input variables, and the empirical relationship between the response and the independent variables in the coded units based on the experimental results was given by

$$Y = 74.4 + 14A + 3.5B + 7C - 1.25AB - 4.25AC + 1.75BC - 26.575A^2 - 14.075B^2 - 13.575C^2$$

The statistical significance of the quadratic model was evaluated by the ANOVA. The results from the ANOVA for the quadratic equation are presented in the Table 3. The ANOVA indicates that the actual relationship between the response and significant variables represented by the above quadratic equations are accurate. The significance of the coefficient term is determined by the values of F and p and the larger the F value and smaller the value of p, the more significant is the co-efficient term. The p is lower than 0.05, suggesting the model to be statistically significant. For the present synthesis process, the ANOVA results indicated the Model F value was 24.68 for *Citrus limonum* oil suggesting only 0.01% chance of a “Model F value” so large could occur due to noise and most of the variation in the response could be explained by the regression equation and the model was significant. In addition, the probability $p<0.0001$ also validated that the model was significant. In the present investigation, A, C, A^2, B^2, C^2 are significant model terms for *Citrus limonum* oil. The other model terms, whose values of p were higher than 0.1000 in Table 3 were not significant.

In a system with different number of independent variables, the adjusted R^2 (Adj-R^2) value is more suited for evaluating the model goodness of fit. In this model, the predicted R^2 0.5759 for *Citrus limonum* oil values are in reasonable agreement with the adjusted R^2 0.9302 values. The results indicated that the selected quadratic model was adequate in assuming the response variables for the experimental data. The perturbation plot can be used to find the most influential factors on the response. A steep slope or curvature in a factor shows that the response is sensitive to that variable.

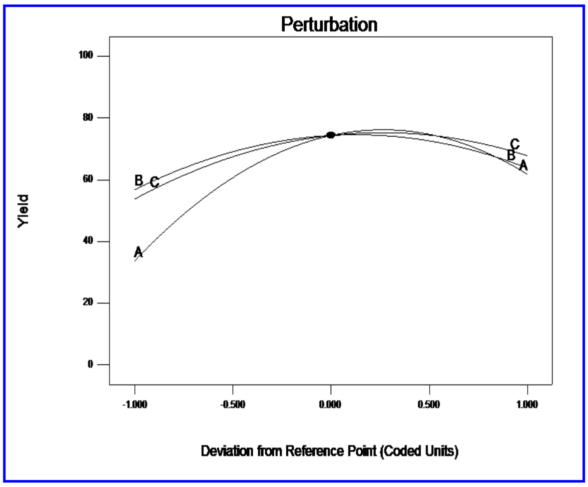

Fig. 1: Perturbation Plot for *Citrus limonum* oil

3.1 Three Dimensional Response surface plots

To study the interaction between all three variables, three dimensional surfaces and two dimensional contours were plotted by keeping one variable constant at central level and the other two varying within the experimental ranges. The full range of two factors at a time can be displayed. In these 3 dimensional graphs a steep slope or curvature in a factor shows that the response is sensitive to that factor. In this experiment, the Fig. 2 indicates that the response is sensitive to the reaction temperature. The yield percentage of MWNTs increases with increase in temperature and attains peak at optimum temperature (650 °C) for *Citrus limonum* oil. Low yield obtained at 550 °C and 750 °C is possibly due to the fact that the catalyst could not be activated and high rate of pyrolysis followed by encapsulation of catalyst respectively. High yield obtained at 650 °C in this study is attributed to almost equal rate of pyrolysis of precursor and CNTs growth (Kumar *et al*. 2005).

The combined effect of temperature and feed rate of carbon precursor on the yield percentage was shown in Fig. 3. As can be understood from the Figure 3 increase of precursor feed rate from 10 mL to 20 mL increases the yield percentage of MWNTs. Further increase of flow rate to 30 mL leads to reduction in the yield of MWNTs. Higher yield obtained for the precursor feed of 20 mL per hour may be attributed to the effective pyrolysis of the precursor at this experimental condition.

3.2 Numerical Optimization

Response surfaces are used to determine an optimum. Table 4 represents the solution for numerical optimization. It is possible that at this temperature the carbon precursor was sufficiently pyrolyzed and good interaction between the hydrocarbon and catalyst facilitated the formation of uniform carbon nanotube diameter. The optimum parameters suggested for the maximum yield of 77.11 through this experiment are reaction temperature 674.29°C, Catalyst composition of 0.53g and the Feed rate of precursor was 22.28mL. SEM and HRTEM image of as grown CNTs under optimized condition was shown in the Fig. 4 & 5. Raman spectrum of the as grown carbon nanotube was shown in the Fig. 6. Two peaks are observed at 1335 cm^{-1} and 1545cm^{-1} corresponds to D peak and G peak. The absence of lower frequency radial breathing modes (RBM) indicated the absence of Singlewalled carbon nanotubes. The I_G/I_D ratio calculated from the peak area is 1.8.

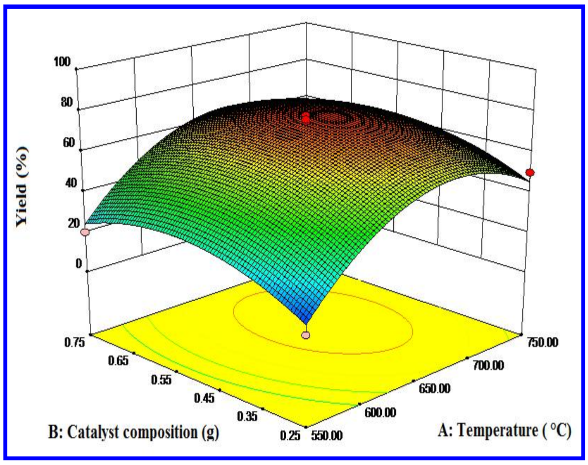

Fig. 2: The response surface plot as the function of temperature and catalyst composition

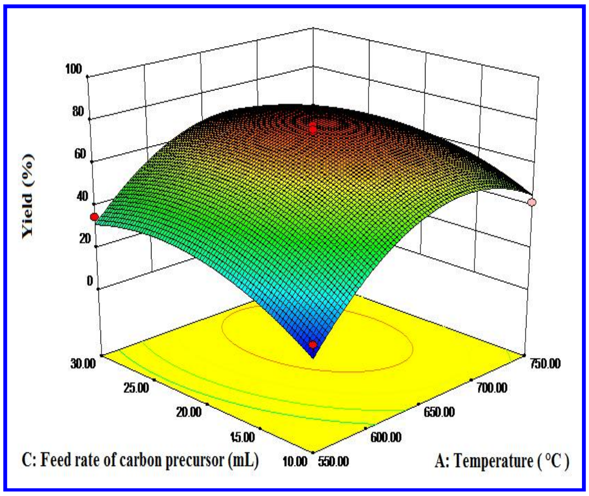

Fig. 3: The response surface plot as the function of temperature and feed rate of carbon precursor

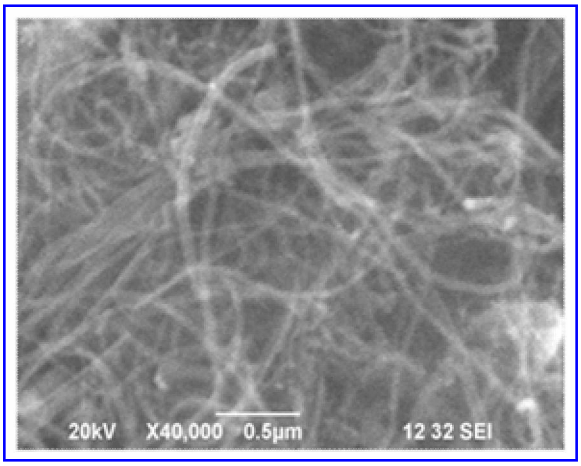

Fig. 4: SEM image of as grown CNT at optimized condition

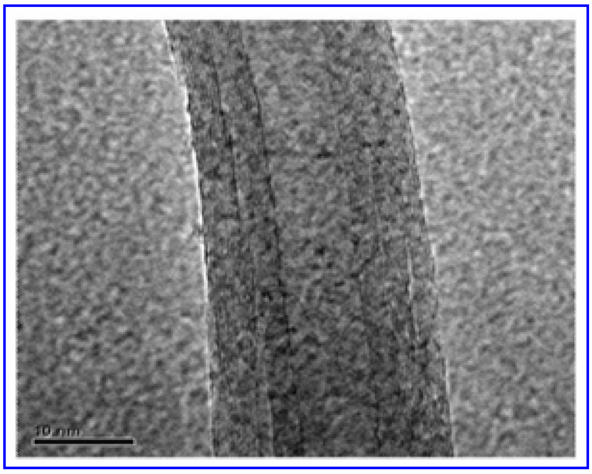

Fig. 5: HRTEM image of as grown CNT at optimized condition

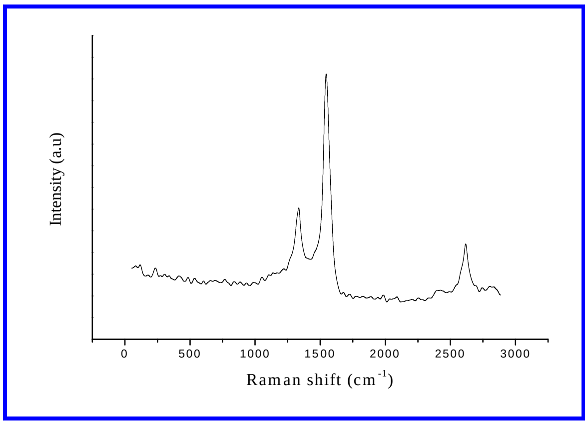

Fig. 6: Raman spectrum of as grown CNT at optimized condition

Table 4. Obtained optimum values of the process variables and responses

Variables	Optimum Values *Citrus limonum* oil
Reaction temp(°C)	674.29
Catalyst composition (g)	0.53
Feed rate of Precursor (mL)	22.28
Yield percentage (Predicted)	77.11
Yield percentage (Actual)	78

4. CONCLUSION

In this study Response surface methodology based Box-Behnken design of experiment was used to optimize the yield of MWCNTs synthesized using *Citrus limonum* oil as the carbon precursor. By implementing the optimal parameters maximum yield of CNT was produced. The optimum parameters suggested through this experiment are reaction temperature 674.29 °C, Catalyst composition of 0.53g and the Feed rate of precursor was 22.28mL. This effective method can be applied to achieve maximum yield of CNT in large scale industries.

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